

Coating composition for metal conductors and coating process involving the use thereof

Background of the Invention

B The invention relates to a coating composition for metal conductors such as, for example, wires, with improved partial discharge resistance and good mechanical properties.

Three-phase a.c. motors, for example, frequency converter-controlled motors or high voltage asynchronous machines require the use of wire wrappings which satisfy the stringent requirements in respect of thermal endurance and the mechanical properties, mainly the flexural strength of the insulation layer, in order to be able to withstand high voltage loads and pulse-shaped voltage loads without damage.

A further requirement in respect of wire wrappings of electrical equipment is the partial discharge resistance of the wire coatings. Adjacent wire wrappings in particular may be exposed to high voltage loads and pulse-shaped voltage loads. For these purposes, the coatings must exhibit a high partial discharge resistance.

According to WO 96/41 909, within the context of a multi-layer coating for wires, a coating composition is used which comprises a binder and a particulate material, wherein the particulate material may be present in the binder in an amount from 1 wt.% to 65 wt.% and may be metal oxides, for example, titanium dioxide, zirconium oxide, zinc oxide, iron oxide or aluminas. The particulate material has no chemical reactivity whatsoever. During the manufacture of such coated wires, preliminary extension may occur which leads to destruction of the coating layers and hence to a drastic decrease in the partial discharge resistance.

Similar compositions with comparable properties are described in DE-A 198 32 186.

According to DE-A 196 50 288, at least one of the electrically insulating coating layers contains an organically modified silica (hetero)polycondensate prepared by hydrolytic condensation of compounds of silicon and optionally of boron,

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aluminium, phosphorus, tin, lead, the transition metals, lanthanides and actinides, the monomer units being composed essentially of inorganic and organic components which are subsequently crosslinked. The coatings obtained have good thermal shock resistance and surface quality. Good flexibilities are not obtained.

- 5 In the as yet unpublished German patent application 198 11 333.1 of the same Applicant, a partial discharge-resistant coating is proposed which, in addition to binders, also contains element-organic compounds, particularly of silicon, germanium, titanium and zirconium. The organic radicals used are C1 to C20 alkyl radicals or chelating radicals, alkylamine, alkanolamine, acetate, citrate, lactate and/or acetate radicals. The organometallic compounds used are monomeric compounds.

- 15 In the as yet unpublished German application 198 41 977.5, inorganic-organic hybrid polymers are used. The transition from monomeric element-organic compounds to element-organic hybrid polymers leads to a further improvement in the partial discharge resistance of the coating layer in question.

- 20 For stringent requirements, particularly for three-phase a.c. motors in continuous operation and frequency converter-controlled motors, the partial discharge resistance obtained is still in need of improvement.

- 25 The object of the present invention is, therefore, to provide a coating composition for metal conductors, particularly wires, the partial discharge resistance of which is increased compared with the solutions of the prior art, particularly when the coated wire is extended. Moreover, the applicability of the coating composition as a single-layer application or as a coating layer in a multi-layer application, and the surface quality and flexibility of the coating should be improved.

Summary of the invention

- 30 It has become apparent that this object may be achieved by a coating composition which contains

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- 5 A) 1 wt.% to 60 wt.% of one or more reactive nanomers based on an element-oxygen network with elements of the series comprising aluminium, tin, boron, germanium, gallium, lead, the transition metals and the lanthanides and actinides, particularly of the series comprising silicon, titanium, zinc, yttrium, cerium, vanadium, hafnium, zirconium, nickel and/or tantalum,
- B) 0 wt.% to 90 wt.% of one or more conventional binders, and
- C) 0 wt.% to 95 wt.% of one or more conventional additives, solvents, pigments and/or fillers,
- 10 wherein the reactive nanomer of component A is based on the element-oxygen network, on the surface of which reactive functions R_1 and optionally non-reactive and/or partially reactive functions R_2 and R_3 are bound by way of the oxygen of the network,
- 15 R_1 being contained in an amount up to 98 wt.%, preferably up to 40 wt.%, particularly preferably up to 30 wt.%, R_2 and R_3 in an amount from 0 wt.% to 97 wt.%, preferably 0 wt.% to 40 wt.%, particularly preferably 0 wt.% to 10 wt.% in the nanomer according to the invention, in which
- 20 R_1 represents radicals of the metal acid esters such as, e.g., $OTi(OR_4)_3$, $OZr(OR_4)_3$, $OSi(OR_4)_3$, $OSi(R_4)_3$; $OHf(OR_4)_3$; NCO; urethane, epoxide, epoxy, carboxylic acid anhydride; C=C double bond systems such as, e.g., methacrylate, acrylate; OH; alcohols bound by way of oxygen, e.g., bis(1-hydroxymethylpropane)-1-methylolate, 2,2-bis-(hydroxymethyl)-1-propanol-3-propanolate, 2-hydroxypropan-
- 25 1-ol-3-olate, esters, ethers, e.g., 2-hydroxyethanolate, C_2H_4OH , diethylene glycolate, $C_2H_4OC_2H_4OH$, triethylene glycolate, $C_2H_4OC_2H_4OC_2H_4OH$; chelating agents, e.g., aminotriethanolate, aminodiethanolate, acetyl acetate, ethyl acetoacetate, lactate; COOH; NH_2 ; NHR_4 ; and/or esters, reactive resin components such as, e.g., OH-, SH-, COOH-, NCO-, capped NCO-, NH_2 -, epoxy, carboxylic acid anhydride, C=C,
- 30 metal acid esters, silane-containing polyurethanes, polyesters, poly(THEIC) esters, poly(THEIC)ester imides, polyamide imides, polyamides, polysiloxanes, polysulfides, polyvinyl formals, polymers, e.g., polyacrylates.

R_2 represents radicals of aromatic compounds, e.g., phenyl, cresyl, nonylphenyl, aliphatic compounds, e.g., branched, linear, saturated, unsaturated alkyl radicals C1 to C30, fatty acid derivatives; linear or branched esters and/or ethers,

- 5 R_3 represents resin radicals, e.g., polyurethane, polyester, polyester imide, THEIC-polyester imide, polytitanic ester resins and derivatives thereof; polysiloxane resins with organic derivatives; polysulfide, polyamide, polyamide imide, polyvinyl formal resins, and/or polymers such as, e.g., polyacrylates, polyhydantoins,
- 10 polybenzimidazoles, and

- R_4 represents radicals of acrylate, phenol, melamine, polyurethane, polyester, polyester imide, polysulfide, epoxide, polyamide, polyvinyl formal resins; aromatic compounds, e.g., phenyl, cresyl, nonylphenyl; aliphatic compounds, e.g., branched,
- 15 linear, saturated, unsaturated alkyl radicals with C1 to C30; esters; ethers, e.g., methyl glycolate, methyl diglycolate, ethyl glycolate, butyl diglycolate, diethylene glycolate, triethylene glycolate; alcoholates, e.g., 1-hydroxymethyl-propane-1,1-dimethylolate, 2,2-bis-(hydroxymethyl)-1,3-propane diolate, 2-hydroxypropane-1,3-diolate, ethylene glycolate, neopentyl glycolate, hexane diolate, butane diolate; fats,
- 20 e.g., castor oil and/or chelating agents, e.g., aminotriethanolate, aminodiethanolate, acetyl acetate, ethyl acetoacetate, lactate.

Detailed Description of the Invention

- The nanomer of component A) according to the invention is composed of an element-oxygen network on the surface of which the reactive functions R_1 and optionally non-reactive or partially reactive functions R_2 and R_3 are bound by way of
- 25 the oxygen of the network. The nanomers with the described functions R_1 to R_4 are particles whose average radius is in the range from 1 nm to 300 nm, preferably in a range from 2 nm to 80 nm, particularly preferably in a range from 4 nm to 50 nm.
- 30 The nanomer according to the invention is contained in an amount from 1 wt.% to 60 wt.%, preferably 5 wt.% to 30 wt.%, in the coating composition.

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The element-oxygen network of the nanomer according to the invention contains the above-mentioned elements which are bound by way of oxygen. The network may contain one or more identical or different elements in a regular and/or irregular sequence bound to the oxygen in each case.

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The inorganic network preferably contains the elements of the series comprising titanium, silicon, aluminium and/or zirconium.

For example, compounds based on the products Nyacol DP 5480 from Nyacol

10 Products Inc. may be used as component A).

Optionally, organic units such as, e.g., radicals of aromatic compounds, aliphatic compounds, esters, ethers, alcoholates, fats and chelating agents, imides, amides, acrylates may also be implemented in the network of the nanomer according to the

15 invention.

The use of $\text{OTi}(\text{OR}_4)_3$, $\text{OZr}(\text{OR}_4)_3$, acetyl acetate, 2-hydroxyethanolate, diethylene glycolate, OH as function R_1 is preferred.

20 The use of radicals of polyester imides and/or THEIC polyester imide resins as function R_3 is preferred.

The use of acrylate resin, aminotriethanolate, acetyl acetate, polyurethane resin and butyl diglycolate as function R_4 is preferred.

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The radicals R_1 to R_4 in each case may be the same or different.

Examples of the nanomers of component A) which may be used according to the invention are shown in Figures 1 to 4.

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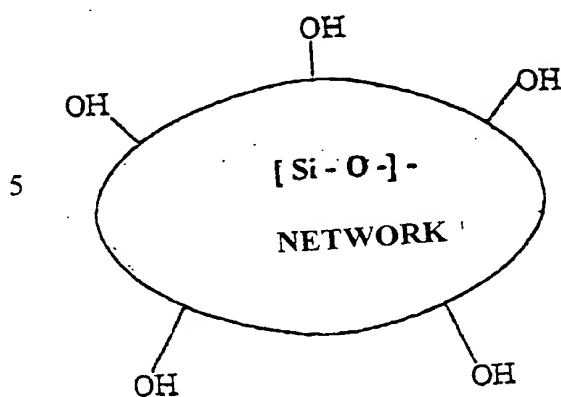


Figure 1

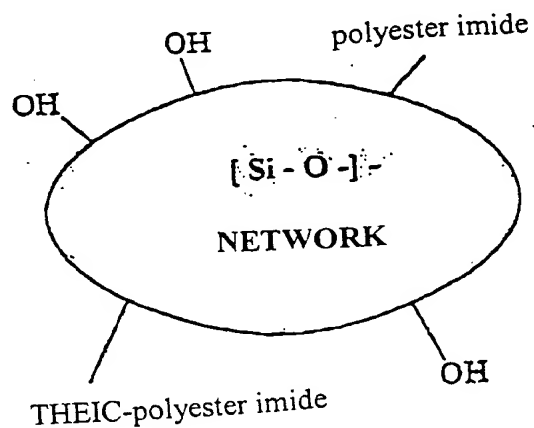


Figure 2

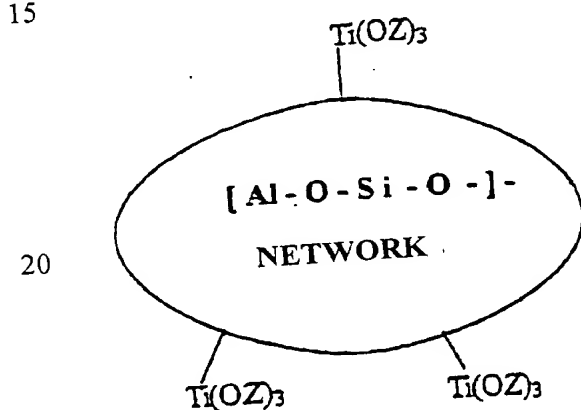


Figure 3

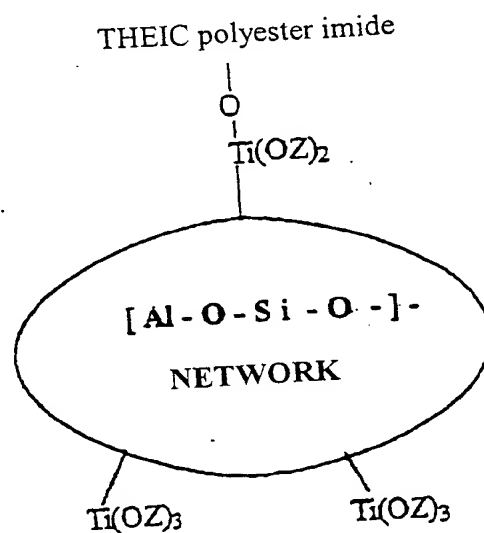


Figure 4

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Figure 1 shows a nanomer which has OH groups as reactive function R_1 . It is able, by way of these OH functions, to react with the corresponding functions of, for example, esters, carboxylic acids, isocyanates, epoxides, anhydrides and the like.

30 The reactivity of the nanomer according to Figure 2 is determined by means of the OH functions as R_1 and the various resin sequences polyester imide and THEIC polyester imide as examples of R_3 .

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The nanomers according to Figures 3 and 4 are provided with ortho-titanic acid ester functions as reactive component R₁. The nanomer according to Figure 4 also has a THEIC polyester imide as polymer fragment R₃.

5 The organic radicals Z stand for isopropyl, butyl, butyldiglycol, triethanolamine, acetyl acetone, polyamide imide, polyurethane and polyester imide groups and aminotriethanolate and epoxide groups, particularly selected from the group comprising R₄.

10 In addition to the nanomers of component A) used according to the invention, monomeric and/or polymeric element-organic compounds may be contained in the coating composition. Examples of polymeric element-organic compounds include inorganic-organic hybrid polymers as mentioned, for example, in the as yet
 15 unpublished German patent application 198 41 977.5. Examples of monomeric element-organic compounds include ortho-titanic acid esters and/or ortho-zirconic acid esters such as, for example, nonyl, cetyl, stearyl, triethanolamine, diethanolamine, acetyl acetone, acetoacetic acid esters, tetra-isopropyl, cresyl, tetrabutyl titanate or zirconate, and titanium tetralactate, hafnium and silicon
 20 compounds, e.g., hafnium tetrabutoxide and tetraethyl silicate and/or various silicone resins.

Additional polymeric and/or monomeric element-organic compounds of this kind may be contained in the composition according to the invention in an amount from
 25 0 wt.% to 70 wt.%.

The preparation of component A) may take place by conventional hydrolysis and condensation reactions of appropriate element-organic or element-halogen compounds in the presence of organic reactants corresponding to functions R₁ to R₃.

30 Similarly, organic resin and/or nanomer components may be reacted with corresponding element-oxide compounds to the corresponding nanomers.

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Such methods of preparation are known to the skilled person, see, e.g., Ralph K. Iler, John Wiley and Sons, "The Chemistry of Silica", New York, p. 312 ff, 1979.

- 5 The composition according to the invention may contain one or more binders as component B) of the kind known and customary in the wire coating sector. Examples include polyesters, polyester imides, polyamides, polyamide imides, THEIC polyester imides, polytitanic acid ester-THEIC ester imides, phenolic resins, melamine resins, polymethacrylimides, polyimides, polybismaleinimides, polyether
- 10 imides, polybenzoxazine diones, polyhydantoins, polyvinyl formals, polyvinyl acetals and/or capped isocyanates. Further binders also include, e.g., epoxides and acrylate resins.

- 15 The use of polyesters and/or polyester imides, particularly THEIC-polyester imides is preferred.

- Polyesters used may include, for example, those that are well known for wire coating. These may also be polyesters with heterocyclic, nitrogen-containing rings, for example, polyesters with imide and hydantoin and benzimidazole structures
- 20 condensed into the molecule.

- The polyesters include, in particular, condensation products of polyvalent, aliphatic, aromatic and/or cycloaliphatic carboxylic acids and anhydrides thereof, polyhydric
- 25 alcohols, in the case of imide-containing polyester amino group-containing compounds optionally with a proportion of monofunctional compounds, for example, monohydric alcohols.

- The saturated polyester imides are based preferably on terephthalic acid polyesters which, in addition to diols, may also contain polyols and, as an additional
- 30 dicarboxylic acid component, a reaction product of diaminodiphenylmethane and trimellitic anhydride.

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Moreover, unsaturated polyester resins and/or polyester imides may also be used. The use of unsaturated polyesters and/or polyester imides is preferred.

Moreover, polyamides may be used as component B), for example, thermoplastic polyamides and polyamide imides of the kind prepared from, e.g., trimellitic anhydride and isocyanatodiphenyl methane. Examples of phenolic resins and/or polyvinyl formals which may be used as component B) include novolaks obtainable by polycondensation of phenols and aldehydes, or polyvinyl formals obtainable from polyvinyl alcohols and aldehydes and/or ketones. Capped isocyanates may also be used as component B), such as, e.g., adducts of polyols, amines, CH-acid compounds (e.g., acetoacetic acid esters, malonic esters i.a.) and diisocyanates, cresols and phenols usually being used as capping agents.

The compositions may contain pigments and/or fillers as component C), for example, colour-imparting inorganic and/or organic pigments such as titanium dioxide or carbon black, and special-effect pigments such as metal flake pigments and/or pearlescent pigments. Examples of additives contained include conventional paint additives, for example, extenders, plasticising components, accelerators (e.g., metal salts, substituted amines), initiators (e.g., photoinitiators, initiators which respond to heat), stabilisers (e.g., hydroquinones, quinones, alkyl phenols, alkyl phenol ethers), defoamers, levelling agents.

In order to increase solubility, the compositions may contain organic solvents such as, for example, aromatic hydrocarbons, N-methylpyrrolidone, cresols, phenols, xylenols, styrenes, vinyl toluene, methyl acrylates. The compositions according to the invention may contain, for example, 30 wt.% to 95 wt.% of organic solvents.

Optionally, the composition according to the invention may also be mixed with conventional wire coatings and then applied by conventional methods.

The application of the composition according to the invention may take place by conventional methods irrespective of the type and diameter of the wire used. The

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wire may be coated directly with the composition according to the invention and then stoved in an oven. Coating and stoving may optionally take place several times in succession. The ovens may be arranged horizontally or vertically, the coating conditions such as duration and number of coatings, stoving temperature, coating speed depending on the nature of the wire to be coated. For example, the coating temperatures may be in the range from room temperature to 400 °C. Moreover, ambient temperatures above 400 °C, for example, up to 800 °C and above may also be possible during coating without any discernable deterioration in the quality of the coating according to the invention.

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During the stoving process, the components of the composition according to the invention, particularly component A) and component B) may undergo a chemical reaction with one another. Depending on the chemical nature of components A) and B), various chemical reactions are possible, for example, transesterification reactions, polymerisation reactions, addition reactions, condensation reactions. According to the preferred use of components A) and B), condensation reactions may take place preferentially.

The use of the composition according to the invention may take place irrespective of the nature and diameter of the wire; for example, wires with a diameter from 5 µm to 6 mm may be coated. Suitable wires include conventional metal conductors, for example, of copper, aluminium, zinc, iron, gold, silver or alloys thereof.

The coating composition according to the invention may be contained as a constituent of a multi-layer coating of the wire. This multi-layer coating may contain at least one coating composition according to the invention.

According to the invention, the wires may be coated with or without coatings already present. Existing coatings may include, for example, insulation coatings and flame retardant coatings. In such cases, the layer thickness of the coating according to the invention may differ considerably.

It is also possible to undertake further coatings by way of the coating according to the invention, for example, further insulation coatings. Such coatings may also be used, e.g., as a top coat for improved mechanical protection and for the creation of desired surface properties and for smoothing. For example, compositions based on polyamides, polyamide imides and polyimides are particularly suitable as top coats.

More particularly, the composition according to the invention is also suitable as a one-coat application.

According to the invention, the composition may be applied in conventional layer thicknesses. It is also possible to apply thin layers without affecting the partial discharge resistance obtained according to the invention, and the adhesion, strength and extensibility of the coatings. The dry layer thickness may vary in accordance with the standardised values for thin and thick wires.

The coatings obtained with the composition according to the invention permit an increased partial discharge resistance of the coating compared with the compositions known hitherto, as a result of which continuous loading under the effect of high voltages, particularly pulse-shaped voltages, becomes possible. They are characterised by a high continuous loading capability and a long service life compared with the coatings based on monomeric and/or polymeric element-organic compounds alone. The partial discharge resistance of the coated wires may be increased so that these are particularly suitable for use with high voltage loads and loads of pulse-shaped high voltages.

The invention is illustrated on the basis of the examples below:

Preparation of a wire coating according to the prior art

Example 1a (comparison)

261.2 g of tris-(2-hydroxyethyl)-isocyanurate (THEIC), 93.2 g of ethylene glycol, 194.2 g of dimethyl terephthalate (DMT) and 0.5 g of zinc acetate were heated to

210 °C within a period of 4 hours in a 2 litre three-necked flask with stirrer, thermometer and distillation unit. 60 g of methanol were distilled. After cooling to 150 °C, 192.1 g of trimellitic anhydride (TMA) and 99.0 g of methylene dianiline (DADM) were added. The mixture was heated with stirring to 220 °C within a
5 period of 3 hours and kept at this temperature for a further 3 hours. 33 g of water were distilled. The mixture was then cooled to 180 °C and 500 g of cresol were added.

With further stirring, a ready to use formulation of the resin solution present was
10 prepared with 882.0 g of cresol, 273.0 g of Solvesso 100, 100.0 g of xylene, 9.0 g of a commercial phenolic resin A, 45.0 g of a commercial phenolic resin B and 18.0 g of ortho-titanic acid-tetrabutylester.

The resulting wire coating had a solids content of 31.3% and a viscosity of
15 410 mPas.

Example 1 b (comparison)

140 g of a particulate SiO₂ material according to WO 96/41 909 and 320 g of cresol
20 were added to 1800 g of the wire coating according to Example 1a and stirred for 60 minutes. A coating dispersion with a solids content of 30.3% and a viscosity of 530 mPas was obtained.

Preparation of wire coatings according to the invention

25 Example 2

200 g of "Nyacol DP 5480" (Si-O nanomer with OH functions, 30% in ethylene glycol, nanomer radius: 25 nm, from Nycol Products Inc.) were added with vigorous
30 stirring to 1800 g of the wire coating according to Example 1a and stirred for 60 minutes. A coating dispersion with a solids content of 30.9% and a viscosity of 390 mPas was obtained.

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Example 3

400 g of "Nyacol DP 5480" were added with vigorous stirring to 1600 g of the wire coating according to Example 1 a and stirred for 60 minutes. A coating dispersion
5 with a solids content of 30.6% and a viscosity of 370 mPas was obtained.

Example 4

10 In a 2 litre three-necked flask with stirrer, thermometer and distillation unit, 130.5 g of tris-(2-hydroxyethyl)-isocyanurate (THEIC), 62.0 g of ethylene glycol, 194.2 g of dimethyl terephthalate (DMT) were mixed thoroughly with 180.0 g of an OH-functional Si-O nanomer (average radius: 25 nm) prepared in the manner described by Ralph K. Iller, loc. cit., at 70°C to 80 °C with vigorous stirring and then heated
15 with 0.5 g of zinc acetate to 210 °C within a period of 4 hours. 60 g of methanol were distilled. After cooling to 150 °C, 192.1 g of trimellitic anhydride (TMA) and 99.0 g of methylene dianiline (DADM) were added. The mixture was heated to 220 °C within a period of 3 hours, with stirring, and kept at this temperature for a further 3 hours. 33 g of water were distilled. The mixture was then cooled to 180 °C and 500.0 g of cresol were added.

20 With further stirring, a ready to use formulation of the resin solution present was prepared with 900.0 g of cresol, 284.5 g of Solvesso 100, 100.0 g of xylene, 9.2 g of a commercial phenolic resin A, 46.2 g of a commercial phenolic resin B and 18.4 g of ortho-titanic acid-tetrabutylester.

25 The resulting wire coating had a solids content of 30.8% and a viscosity of 380 mPas.

Example 5

30 In a 2 litre three-necked flask with stirrer, thermometer and distillation unit, 261.2 g of tris-(2-hydroxyethyl)-isocyanurate (THEIC), 93.2 g of ethylene glycol, 194.2 g of

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- dimethyl terephthalate (DMT) and 0.5 g of zinc acetate were heated to 210 °C within a period of 4 hours. 60 g of methanol were distilled. After cooling to 150 °C, 192.1 g of trimellitic anhydride (TMA) and 99.0 g of methylene dianiline (DADM) were added. The mixture was heated to 220 °C within a period of 3 hours, with stirring, and kept at this temperature for a further 3 hours. 33 g of water were distilled. The mixture was then cooled to 180 °C and 500 g of cresol were added. 45.0 g of ortho-titanic acid-tetra-isopropyl ester were added at 60 °C to 80 °C and, with vigorous stirring, 190.0 g of an OH-functional Al-O-Si-O nanomer (average radius: 20 nm) prepared in the manner described by Ralph K. Iler, loc. cit., and heated to 205 °C within a period of 5 hours, and 38.2 g of isopropanol were distilled. After cooling and with further stirring, a ready to use formulation of the resin solution present was prepared with 1100.0 g of cresol, 355.0 g of Solvesso 100, 129.0 g of xylene, 11.0 g of a commercial phenolic resin A, 50.0 g of a commercial phenolic resin B.
- The resulting wire coating had a solids content of 30.5% and a viscosity of 370 mPas.

Tests:

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| | Solids content 1 g, 1 h, 180 °C [%]. | DIN EN ISO 3251 |
| 20 | Viscosity at 25 °C [mPas] or [Pas] | DIN 53015 |

Application

- Copper wires with a bare wire thickness of 0.3 mm were coated on a conventional wire coating plant with the wire coatings described according to Examples 2 to 5 and Comparison Examples 1a and 1b (single-layer coating). The resulting layer thickness was 18 µm.

Table 1: Technical data of the coated copper wires (according to DIN 46453 and DIN EN 60851)

	Comparison Example 1a	Comparison Example 1b	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Softening Point	394 °C	396	402 °C	404 °C	357 °C	402 °C
Thermal shock 1 x d	220 °C	220 °C	220 °C	220 °C	220 °C	220 °C
Adhesion and extensibility during wrapping 1 x d	25 %	10 %	20 %	15 %	20 %	15 %
Pencil hardness	3-4 H	4-5 H	6-7 H	6-7 H	6-7 H	6-7 H
Paintability	Satisfactory	Satisfactory	Satis.	Satis.	Satis.	Satis.
Service life on converter*	0.8 h	> 1000 h	> 1000 h	> 1000 h	> 1000 h	> 1000 h
Service life on converter*	0.5 h	390	80 h	420 h	480 h	430 h
With 5% pre- extension of coated wire	0.3 h	21 h	70 h	430 h	490 h	410 h
With 10% pre- extension of coated wire	02 h	13 h	60 h	430 h	500 h	430 h

- 5 430 h * frequency converter from Siemens: Simovert P 6SE2103-3AA01
Output: 2.8 kVA, cycle frequency: 10 kHz